

Accounting for greenhouse gas emissions from the degradation of chemicals in the environment

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Abstract

Purpose The degradation of chemicals in the environment is often excluded from life cycle assessment (LCA) studies. This paper describes a method to account for greenhouse gas (GHG) emissions from degradation, namely carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O).

Materials and methods A multi-media fate model is proposed to estimate the distribution and degradation of chemicals released to the environment. The environmental distribution, along with emission factors and assumptions for each compartment (air, water, soil and sediments), is used to calculate emissions of CO₂, CH₄ and N₂O associated with the initial release of a chemical to either the air, water or soil compartments. These emissions, along with global warming potentials (GWP), are converted to CO₂ equivalents from degradation (GWP_{deg}). The method is described and evaluated with nine organic chemicals.

Results and discussion Applying the proposed method to the example chemicals shows that all the end products (CO₂, CH₄ and N₂O) have the potential to significantly contribute to GWP_{deg}, depending on the chemicals' composition and environmental fate. These emissions, taken to represent the end-of-life stage of these nine chemicals, are shown to be significant when compared with the corresponding cradle-to-gate emissions. For three of the nine chemicals, the

degradation emissions in the environment exceeded the cradle to gate phase.

Conclusions The method enables the accounting of GHG emissions that are currently neglected in many LCA and carbon footprint studies. The model has been parameterized for a generic environmental scenario, but it can be adapted for more site-specific conditions. Uncertainty in this method is associated to the potential lack of chemical-specific data to use in fate modelling, the generic evaluative environment used in fate models and the uncertainty associated with emission factors. A Monte Carlo analysis on the latter shows that the highest uncertainty is expected for chemicals where N₂O emissions are the main contributor to GWP_{deg}.

Keywords Carbon footprint · Degradation · End of life · Environmental fate · Indirect effects · Life cycle assessment (LCA) · Life cycle impact assessment

1 Introduction

Assessing cumulative greenhouse gas (GHG) emissions constitutes an essential part of life cycle assessment (LCA) studies. Furthermore, in recent years, an increased market demand for climate-relevant information along supply chains and towards consumers has led to numerous initiatives promoting carbon footprinting, the latter consisting of a more or less simplified version of LCA, where the focus is exclusively put on GHG emissions (Finkbeiner 2009). As a consequence, there is an increasing trend to calculate and report GHG emissions of products and services, with the purposes ranging from labelling (De Koning et al. 2010) to identifying emission reduction opportunities (Milà i Canals et al. 2011).

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In a cradle-to-grave approach, GHG emissions need to be inventoried across all life cycle stages, from resource extraction to product disposal. With regard to the latter, inventories and allocation models have been developed for waste treatment processes such as landfilling, incineration, biological treatment, wastewater treatment and even for human excretion (Dalemo 1997; Sonesson 1997; Muñoz et al. 2008; Doka 2007). In addition to accounting for inputs such as energy and auxiliary materials, all these models attempt to estimate the emissions, including GHG, produced by the degradation of the product, e.g. in a wastewater treatment plant. Nevertheless, there are cases in which waste materials are directly discharged to the environment, due to either the absence of a disposal infrastructure, incomplete degradation during the disposal process, or because this is the way the product is used (e.g. pesticides). In these cases, degradation may take place in the receiving environmental compartments (air, soil, water and sediments), and chemicals containing carbon and nitrogen will contribute to the formation of GHG emissions, through the formation of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). The amounts of these GHG emissions will depend on the mode of entry to the environment, the conditions in the different environmental compartments and the specific properties of the chemical.

In practice, GHG emissions from the degradation of chemicals in the environment are seldom accounted for in LCA studies. To our knowledge, the only exception is the Environmental Design of Industrial Products method (Hauschild and Wenzel 1998) which includes characterisation factors for certain chemicals released to air, such as hydrocarbons eventually breaking down into CO_2 in the atmosphere. However, this method omits the contribution to GHG formation from chemicals released to water and soil, as well as CH_4 and N_2O as potential degradation products. In this work, we address this methodological gap by providing a method for LCA to account for GHG emissions produced by the degradation of chemicals in the environment (Fig. 1).

2 Materials and methods

2.1 Scope, choices and main assumptions

The method we present is described as an impact assessment method and is consistent with how the boundaries between the product system and the environment are set in LCA (ISO 2006; European Commission 2010, p. 275). The method basically consists of a set of equations to quantify emissions of CO_2 , CH_4 and N_2O , similarly as it would be done in the inventory phase of an LCA. GWP are then applied to convert these emissions to CO_2 equivalents, and the final result

of this calculation is the equivalent of a characterization factor.

2.1.1 Applicability of the method

The method is suitable for organic chemicals that degrade into CO_2 , CH_4 or N_2O . Inorganic chemicals containing carbon, such as carbonates, are not a source of either CO_2 or CH_4 and thus are omitted. Carbonates are not degradable, and in water, they tend to increase the pH, whereas the formation of CO_2 is favoured by the opposite effect. Therefore, the formation of CO_2 due to the disturbance of the carbonate equilibrium in the environment can be attributed to acidifying substances, as previously suggested by Hauschild and Wenzel (1998). On the other hand, inorganic sources of nitrogen such as ammonia and nitrogen oxides that may form N_2O in soils, rivers and lakes (Gillenwater et al. 2006) are considered.

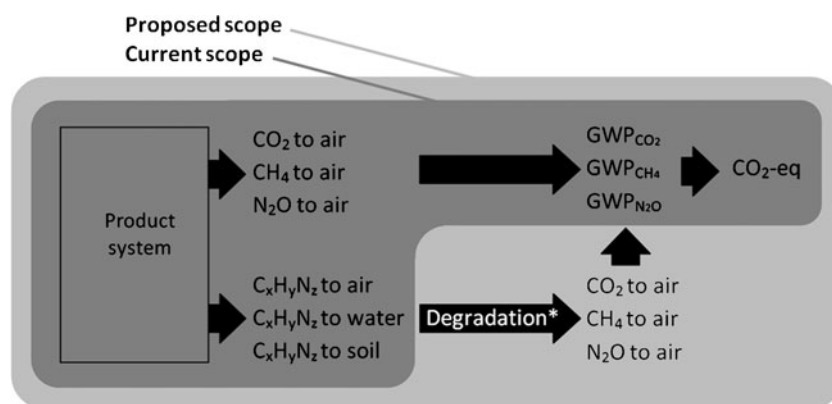
2.1.2 Environmental fate modelling

Equations are provided to calculate GHG emissions for the entry compartments air, soil and water of a generic modelled environment. Sediments are considered in environmental partitioning, but are not considered as an initial entry compartment. In the particular case of the soil compartment, care must be taken to avoid double counting of emissions since in agricultural LCA, soil can be considered as part of the technosphere until harvest (Audsley 1997).

The generic environment considered includes degradation in the four bulk compartments air, water, soil and sediment. We have made the following assumptions for each compartment:

- Air is an aerobic compartment.
- Soil typically consists of 25 % air by volume (Lal and Shukla 2004). Temperate and tropical oxic soils that are continually emerged constitute CH_4 sinks rather than sources (Le Mer and Roger 2001). On the other hand, flooded soils such as paddy rice fields and wetlands are net CH_4 producers. In the model, we have considered only soils that are oxic and emerged; therefore, CH_4 emissions are not considered. A chemical that is released to flooded soils, either natural or cultured, should be treated in the model as a release to water rather than to soil.
- Sediments are considered to be primarily anaerobic (Baird and Cann 2005). However, they generally have a thin aerobic top layer, and this is taken into account in the calculations by means of an oxidation factor (f_{ox}).
- The water compartment is mainly aerobic, although rivers, lakes and estuaries subject to high loads of organic matter may become anaerobic. The Intergovernmental Panel on Climate Change (IPCC) considers, based on expert

Fig. 1 Current and proposed scopes for greenhouse gas accounting. *See Fig. A.1 in the ESM for a conceptual diagram on fate and degradation modelling



judgement, an average anaerobic fraction of 10 % (Doom et al. 2006). The model therefore assumes the water compartment to be 90 % aerobic and 10 % anaerobic. This can be adjusted as necessary to reflect other conditions.

- No degradation emissions are taken into account due to the metabolism of chemicals' uptake by plants. However, degradation in the root zone is included, as this is considered part of the soil compartment. It has been suggested that terrestrial plants can emit methane under aerobic conditions, but there is still a lack of understanding of the mechanism, and a debate around the relative magnitude of this source in the global methane budget (Keppler et al. 2006; Nisbet et al. 2009).

In the equations, CH₄ is linked to anaerobic conditions only. As for N₂O, its formation is not linked to the redox conditions since it is produced during both nitrification (aerobic conditions) and denitrification (anoxic conditions) (Gillenwater et al. 2006). For a conceptual overview of this generic environment, see Fig. A.1 in the Electronic supplementary material (ESM).

The distribution and degradation of chemicals in the environment are determined using a multi-media fate model. Several such models, initially developed for risk assessment, have been used in the LCIA context. Some examples are the Uniform System for the Evaluation of Substances adapted for LCA purposes (USES-LCA; Huijbregts et al. 2005), Caltox (McKone et al. 2002), EUSES (Goedkoop and Spriensma 2000) and USEtox (Rosenbaum et al. 2008). Being a 'consensus' model (Hauschild et al. 2008), USEtox is positioning itself as the preferred model for the assessment of toxicity impacts in LCA; however, its fate modelling component is not suited for our approach as it lacks a separate sediment compartment.

2.1.3 Degradability of organic chemicals

Our method estimates the degradation of organic chemicals to end products such as CO₂, and as a consequence, degradation is better represented by ultimate degradation rates

(mineralization) rather than primary degradation rates (parent compound removal). The former should be used as input whenever available.

For some highly recalcitrant organic chemicals, the time required for complete degradation can be very long. If a chemical is removed from the system without degradation by e.g. burial in deep sediments, then we do not attribute any GHG formation to its release. On the other hand, a chemical removed by advection from the troposphere to the stratosphere is treated in the model as degraded in air since the chemical is expected to be depleted through photolysis and oxidation with hydroxyl radicals (OH·) (Mohanakumar 2008, p.227). In practice, though, it is expected that only a limited number of chemicals will be persistent enough to show significant removal from the system.

Also, the degradation of some recalcitrant chemicals in the environment depends on the presence of an additional substrate that is degraded at the same time (co-metabolism). The recalcitrant chemical could then be allocated the GHG emissions from degradation of both compounds. In our approach, there is no discrimination of metabolic and co-metabolic degradation of chemicals, and potential GHG emissions from additional substrates are not taken into account.

2.1.4 Time boundary and consideration of delayed emissions

There is no time cutoff for the accounting of degradation and its derived GHG emissions. The extent of degradation of a chemical is estimated modelling a system in steady-state, and is thus time-independent.

Delayed emissions are those taking place years after the formation of the product. The PAS 2050, for example, considers as delayed emissions those from the use phase or disposal phase taking place after 1 year of the product formation (BSI 2008). As mentioned in the previous section, some chemicals can take years to achieve full degradation, leading to such delayed GHG emissions. There is an increasing interest on being able to address this delay if required (Clift and

Brandão 2008; BSI 2008; Levasseur et al. 2010; European Commission 2010); however, a general consensus on how to do this has not been achieved. In this paper, there is no specific allowance for delayed emissions, and hence, all emissions are assumed to occur at time 0. However, the input data used would allow a user to take the effect of delayed emissions into account if required. In order to do this, the half-lives of a chemical in each compartment, along with its partitioning profile, could be used to build a dynamic, i.e. time-dependent, GHG emission profile. Such a profile could be converted to discounted CO₂-eq emissions with available tools like the one developed by Levasseur (2011).

2.1.5 Carbon accounting, methane oxidation and global warming potentials

Carbon accounting, and particularly biogenic¹ carbon accounting, is a controversial topic in LCA. It is common to assume that CO₂ originating from biomass is not a net contributor to global warming, and although reported in inventories, it is usually assigned a GWP of 0 (Rypdal et al. 2006). Nevertheless, the recently published ILCD handbook advocates for an equal treatment of CO₂ emissions, regardless of their origin (European Commission 2010, p. 226). Table 1 summarizes the direct GWP-100 values that can be used in any LCA for CO₂ and CH₄, with two approaches: if biogenic CO₂ emissions are assigned a GWP of 1 or a GWP of 0. In the ESM, we provide further explanations and quantitative examples demonstrating that both approaches lead to the same results. However, these GWP values are not entirely consistent with the approach we propose as they refer to the direct contribution to global warming, i.e. through radiative forcing, whereas our purpose is to include the indirect contribution from degradation. For our method to be consistent, the oxidation of CH₄ needs to be taken into account, in the same way as it is for any other organic chemical, but if this is done in the inventory analysis, it would lead to double counting. As a consequence, the proposed solution is to account for this oxidation in the impact assessment stage, by increasing the GWP of CH₄, as shown in Table 1 (direct+indirect). For further details, see the ESM.

CH₄ is not the only GHG for which degradation could be considered. All organic GHG (chlorofluorocarbons, hydrofluorocarbons, fluorinated ethers, etc.) could be subject to similar adjustments; however, given their relatively high direct GWP values (usually above 1,000 kg CO₂-eq kg⁻¹), the indirect contribution from degradation is negligible.

¹ Recently derived from biomass, i.e. plant or animal sources, as opposed to fossil sources, e.g. peat, coal, oil, etc.

2.2 Equations

2.2.1 General equation

The characterization factor for a chemical x released to an environmental compartment y is expressed as its GWP from degradation (GWP_{deg}) in kilograms CO₂-eq per kilogram of chemical. It is calculated with Eq. (1):

$$GWP_{deg,x,y} = E_{CH_4,x,y} \cdot GWP_{CH_4} + E_{CO_2,x,y} \cdot GWP_{CO_2} + E_{N_2O,x,y} \cdot GWP_{N_2O} + E_{CO_2-seq,x,y} \cdot GWP_{CO_2-seq} \quad (1)$$

Where E_{CH_4} , E_{CO_2} and E_{N_2O} are the CH₄, CO₂ and N₂O emissions, respectively, resulting from degradation of chemical x released to compartment y (air, water or soil), in kilograms per kilogram. E_{CO_2-seq} is the carbon sequestration in the environment, expressed as a negative CO₂ emission. GWP_{CH_4} , GWP_{CO_2} , GWP_{CO_2-seq} and GWP_{N_2O} are the GWP values attributed to these four emissions in kilograms CO₂-eq per kilogram. In the case of CH₄, the GWP must include the direct and indirect contributions (see Table 1). Table 1 is based on GWP values for 100 years, but it could be re-elaborated for other time horizons, like 20 or 500 years.

2.2.2 CH₄

CH₄ emissions are produced in only two compartments: water and sediments. They are calculated using Eq. (2):

$$E_{CH_4,x,y} = C_x \cdot f_{CH_4} \cdot \left(Deg_{w,x,y} \cdot MCF_w + Deg_{sed,x,y} \cdot MCF_{sed} \right) \cdot \frac{16}{12} \quad (2)$$

Where C_x is the carbon content in the chemical (kilograms per kilogram), and f_{CH_4} is the fraction of carbon that is converted to CH₄ under anaerobic conditions. Based on typical CH₄ content in biogas, this parameter ranges from 0.5 to almost 0.8 (Dalemo 1997). A generic value of 0.6 is used for this parameter. $Deg_{w,x,y}$ and $Deg_{sed,x,y}$ are the fractions of chemical x released to compartment y that are degraded in water and sediments, respectively, according to the fate model. MCF_w and MCF_{sed} are the methane correction factors for the water and sediment compartments, respectively. These parameters measure the extent of anaerobicity in both compartments. MCF_w takes a value of 0.1 (Doorn et al. 2006), whereas for sediments, it is calculated with Eq. (3):

$$MCF_{sed} = 1 - f_{ox} \quad (3)$$

Where f_{ox} is the fraction of CH₄ produced in the sediments that is converted to CO₂ by microbial oxidation in the upper

Table 1 GWP-100 values assigned to different GHG, depending on how biogenic carbon is accounted for and on the inclusion/exclusion of CH₄ oxidation

GHG	GWP-100 (kg CO ₂ -eq kg ⁻¹)			
	Direct ^a		Direct+indirect ^b	
	Biogenic CO ₂ neutral	Biogenic CO ₂ not neutral	Biogenic CO ₂ neutral	Biogenic CO ₂ not neutral
CO ₂ incorporated in biomass	0	−1	0	−1
CO ₂ biogenic emitted	0	1	0	1
CO ₂ biogenic sequestered	−1	0	−1	0
CO ₂ fossil emitted	1	1	1	1
CO ₂ fossil sequestered	0	0	0	0
CH ₄ biogenic emitted	22.25	25	25	27.75
CH ₄ fossil emitted	25	25	27.75	27.75
N ₂ O	298	298	298	298

^a GWP due to radiative forcing only, with the exception of CH₄ which includes indirect effects other than oxidation to CO₂

^b Indirect contribution to GWP is only relevant for CH₄ and considers its oxidation to CO₂

layers of sediments. In order to define a value for this parameter, a literature search was carried out (see [ESM](#)). Based on the widely variable data available, a generic value of 0.5 (50 % oxidation) is suggested.

2.2.3 CO₂

CO₂ is produced to some extent in all compartments (air, water, soil and sediments). Emissions are calculated using Eq. (4):

$$E_{CO_2,x,y} = C_x \cdot \left[\frac{Deg_{a,x,y} + Deg_{w,x,y} \cdot (1 - MCF_w \cdot f_{CH_4}) + Deg_{sed,x,y} \cdot (1 + f_{CH_4} \cdot (f_{ox} - 1)) + Deg_{s,x,y}}{44/12} \right] \quad (4)$$

Where $Deg_{a,x,y}$ and $Deg_{s,x,y}$ are the fractions of chemical x , released to compartment y , that are degraded in air and soil, respectively. If full degradation is not expected, the remaining fraction is accounted for as a carbon sequestration, which is calculated as CO₂-eq using Eq. (5):

$$E_{CO_2-seq,x,y} = C_x \cdot \left(1 - Deg_{a,x,y} - Deg_{w,x,y} - Deg_{sed,x,y} - Deg_{s,x,y} \right) \cdot \frac{44}{12} \quad (5)$$

2.2.4 N₂O

N₂O occurs as a result of nitrification and denitrification in soils and the surface of rivers, lakes and other waters.

Organic and inorganic N can reach any of these environmental compartments directly or indirectly through environmental transport. Emissions are calculated with Eq. (6):

$$E_{N_2O,x,y} = N_x \cdot \left(\frac{Deg_{a,x,y} \cdot EF_a + Deg_{s,x,y} \cdot EF_s + Deg_{w,x,y} \cdot EF_w + Deg_{sed,x,y} \cdot EF_{sed}}{44/28} \right) \quad (6)$$

Where N_x is the nitrogen content in the chemical (kilograms per kilogram), and EF_a , EF_s , EF_w and EF_{sed} are the N₂O emission factors for the air, soil, water and sediment compartments, respectively (kilograms N-N₂O per kilogram N⁻¹). Both EF_a and EF_s take a value of 0.01, based on the fact that the emission factor for direct emissions of N₂O from managed soils according to the IPCC (EF_1 in De Klein et al. 2006, Table 11.1) has the same value as that proposed for N₂O emissions from volatilized N that re-deposits in the environment (EF_4 in De Klein et al. 2006, Table 11.3). Concerning EF_w , the IPCC guidelines consider a value of 0.005 for wastewater discharges to rivers and estuaries (Doorn et al. 2006, section 6.3.1.2). There is no separate emission factor for sediments in the IPCC guidelines, although according to Nevison (2000), this same value has been previously assumed for both compartments and is used for EF_{sed} in Eq. (6).

In the case of inorganic chemicals containing N, there is no degradation as such, but speciation upon entrance in the environment. Also, fate models cannot be used with inorganic chemicals, resulting in the impossibility of predicting the Deg parameters required in Eq. 6. In order to overcome this limitation, it is proposed to use Eq. 6 assuming that the initial release compartment is also the final environmental compartment. This approach for inorganic N leads to the

same results than the Tier 1 IPCC methods when the initial release compartment is either air or water, but can result in an underestimation when N is applied to soil since N_2O contributions from N redistribution through volatilization and leaching are omitted.

2.3 Application to a group of chemicals

The proposed method was tested with nine industrial chemicals selected based on their range of physical–chemical properties and degradation rates (see [ESM](#)). In case of chemical-specific data gaps, the EPI Suite program v.4.1 was used (USEPA 2009). The fate model in USES-LCA was chosen to obtain values for the *Deg* parameters in Eqs. 2, 4, 5 and 6, as follows:

- The fraction degraded in air (Deg_a) was taken as the sum of the fractions degraded in all the air compartments (regional, continental and global scales) plus the fraction of chemical advected to the stratosphere.
- The fraction degraded in water (Deg_w) was taken as the sum of the fractions degraded in fresh water and sea water of all the surface water compartments (regional, continental and global scales) plus the fraction leached to groundwater.
- The fraction degraded in soil (Deg_s) was taken as the sum of the fractions degraded in all the soil compartments (regional, continental and global scales).
- The fraction degraded in sediments (Deg_{sed}) was taken as the sum of the fractions degraded in fresh water and sea water sediment compartments (regional, continental and global scales).

As mentioned in Section 2.1.2, degradation in vegetation is not included in our method. However, this degradation pathway is included in USES-LCA. In the case study, this process was disregarded, by assuming a degradation rate in plants of $0 (1e^{-20})s^{-1}$ for all chemicals.

The entry compartments considered for the nine chemicals were air, fresh water and agricultural soil. USES-LCA includes other entry compartments such as natural soil or sea water, which were not taken into account in the case study.

GWP values used in Eq. 1 for CO_2 , CH_4 and N_2O were calculated including direct and indirect contributions, and biogenic CO_2 was considered neutral. The calculated GWP_{deg} values from Eq. 1 were then compared to the GWP associated with producing the chemicals (cradle to gate boundaries), using the data sources in Table 2. In case of multiple data sources, the average value was used.

Degradation emissions for chemicals emitted in the cradle-to-gate stages of the nine tested chemicals were not considered. However, CH_4 oxidation was taken into account in all life cycle stages by increasing the GWP used for this gas, as discussed in Section 2.1.5.

As part of the case study, a probabilistic analysis by means of Monte Carlo simulations was carried out to obtain an estimate of the uncertainty around the mean GWP_{deg} values calculated for the nine organic chemicals. Uncertainty was considered for seven parameters used in the equations, namely MCF_w , f_{ox} , f_{CH_4} , EF_a , EF_s , EF_w and EF_{sed} . Probability distribution functions were defined for each parameter based on the available data (see Table A.8 in the [ESM](#)). The Monte Carlo simulations were performed with the @RISK software (Palisade Corporation 2008). Three simulations per chemical were carried out (one per entry compartment, i.e. air, water and soil), each consisting of 10,000 iterations. In this analysis, uncertainties associated with the following components were not included: chemical-specific data, fate modelling with USES-LCA and GWP values.

3 Results and discussion

3.1 Emissions from environmental degradation

GWP_{deg} per kilogram of chemical was calculated for each chemical released to either air, water or soil. The full results are shown in the [ESM](#), whereas in Fig. 2, we show a summary of these by selecting a likely release compartment per chemical. The magnitude of the GWP_{deg} value depends upon the composition of the chemical and the type of degradation. It can be seen in the figure that all the end products (CO_2 , CH_4 and N_2O) have the potential to significantly contribute to GWP_{deg} . However, the carbon sequestration (CO_2 -seq) component in these chemicals is negligible since they are expected to degrade.

In Fig. 2, GWP_{deg} ranges from 0.6 kg CO_2 -eq kg^{-1} for biogenic ethanol released to air to 3.4 kg CO_2 -eq kg^{-1} for FWA-1 released to water. The low value for ethanol is explained by the fact that the main degradation product is biogenic CO_2 , which is not attributed a contribution to global warming. Also, the ethanol molecule has no N atoms to be converted to N_2O . On the other hand, according to USES-LCA, 56 % of the emitted ethanol is expected to be degraded in water, where some of the carbon is converted to CH_4 . This same chemical, when based on fossil feed-stock, is attributed a GWP_{deg} of 2.5 kg CO_2 -eq kg^{-1} , mostly due to the fossil CO_2 emissions. The highest GWP_{deg} value obtained in the calculations corresponds to pendimethalin when emitted to water, with a value of 4.3 kg CO_2 -eq kg^{-1} (see [ESM](#)), mainly due to the CH_4 emissions from degradation in sediments and in the anaerobic fraction of water compartments.

Table 2 Chemicals assessed

Chemical	CAS number	Uses	Carbon origin considered	Data used to cover cradle to gate
Ethanol	64-17-5	Fuel, chemical feedstock, solvent	Biogenic	Ecoinvent 2.2 datasets for ethanol production from sugarcane (Brazil), sugarcane molasses (Brazil), grass (Switzerland), potatoes (Switzerland), sugar beet molasses (Switzerland), sugar beets (Switzerland), whey (Switzerland), wood (Switzerland), sweet sorghum (China), rye (Europe), corn (USA) and biomass (Brazil, Europe, USA) (Jungbluth et al. 2007)
			Fossil	Ecoinvent 2.2 dataset for ethanol production from ethylene (Europe) (Sutter 2007)
Propane	74-98-6	Fuel, chemical feedstock, propellant	Fossil	Ecoinvent 2.2 datasets for propane/butane production in Europe and Switzerland (Dones et al. 2007)
Enzyme (generic)	–	Catalyst	Biogenic	GWP per kg for several enzymes manufactured in Denmark: Termamyl 120 L, Spirizyme plus FG, Ronozyme P5000 CT, Savinase 12 TXT, Novamyl 10000 BG (Nielsen et al. 2007)
Linear alkylbenzene sulfonate (LAS)	25155-30-0	Anionic surfactant	Fossil	Ecoinvent 2.2 dataset for production of linear alkylbenzene sulfonate in Europe (Zah and Hirschier 2007)
Fluorescent whitening agent 1 (FWA-1)	16090-02-1	Fluorescer	Fossil	Ecoinvent 2.2 dataset for production of DAS-1 fluorescent whitening agent in Europe (Zah and Hirschier 2007)
Melamine	108-78-1	Chemical feedstock	Fossil	Ecoinvent 2.2 dataset for production of melamine in Europe (Althaus et al. 2007)
Diuron	330-54-1	Herbicide	Fossil	Ecoinvent 2.2 dataset for production of diuron in Europe and Switzerland (Nemecek et al. 2007)
Pendimethalin	40487-42-1	Herbicide	Fossil	Ecoinvent 2.2 dataset for production of pendimethalin in Europe (Nemecek et al. 2007)

3.2 Comparison of the environmental degradation emissions and the cradle-to-gate emissions

To understand the relevance of emissions from the degradation of the chemicals in the environment, they are compared in

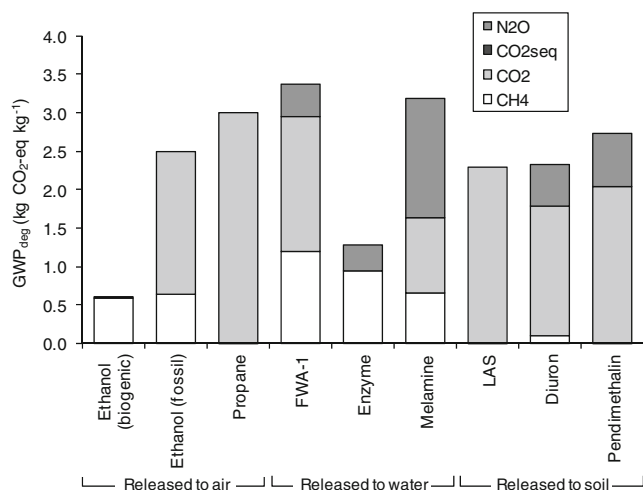


Fig. 2 GWP_{deg} per kilogram chemical for a selection of release compartments. Results for all compartments are available in the [ESM](#)

Fig. 3 to those associated with production of the chemicals (cradle-to-gate boundaries). The GWP_{deg} data in this graph represent the emissions associated to the end-of-life stage for these chemicals, assuming they are released directly to the specified environmental compartment without any treatment.

The GHG emissions from the degradation of the chemicals in the environment are comparable to those associated with the production of the chemicals. For ethanol from a fossil feedstock, propane and linear alkylbenzene sulfonate (LAS), GHG emissions from degradation in the environmental exceed those from their cradle to gate phases. For bio-based ethanol, the reason why GHG emissions are relatively low is that the main degradation product for this chemical, when released to air, is biogenic CO₂, which is attributed no contribution to global warming.

Ethanol in Fig. 3 allows us to see how this method can be used to discriminate between bio-based and fossil-based chemicals. According to ecoinvent data, these two chemicals have on average similar cradle-to-gate emissions, but when the carbon cycle is closed, the overall emissions are lower if biogenic feedstocks are used. This conclusion is reached regardless of how biogenic CO₂ is considered: “neutral” or “not neutral”, according to Table 1.

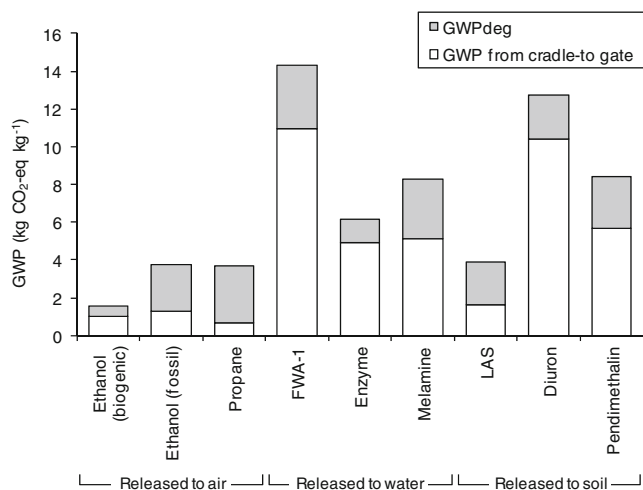


Fig. 3 GWP from cradle-to-gate plus GWP_{deg} associated to end of life, the latter assuming the same release compartment as in Fig. 1; results per kilogram chemical

Currently, these sources of GHG emissions are often not taken into account in LCA studies, and yet missing them can be compared to omit combustion emissions in a cradle-to-grave LCA of fuels. For example, exclusion of such emission in cases such as the industrial or consumer applications where the primary release of the chemical is to the air (e.g. ethanol and butane) would lead to a clear underestimation of global warming impact of such product systems. Similarly, this applies to products that may be used and enter directly into the environment, such as in the case of countries with poor sewerage systems or where there is direct product use such as for washing in a river.

3.3 Uncertainty

We identified three main sources of uncertainty in this method: chemical-specific data, fate modelling and emission factors for N₂O and CH₄. We discuss qualitatively the first two subjects, whereas the uncertainty related to emission factors for N₂O and CH₄ is discussed based on the results of a quantitative Monte Carlo analysis.

3.3.1 Chemical-specific data

For many chemicals, finding complete data on physico-chemical properties and degradability rates in the environment is challenging (Van Hoof et al. 2011). In the absence of experimental data, there is a risk of abusing the use of estimation programs like those in EPI Suite, which require expert judgement to interpret the validity of their outcome. In the case of ionisable substances, it must be borne in mind that these tools predict the properties of the neutral molecule rather than those of the charged molecule, which may be the dominating species in the environment. For example, for

FWA-1, the KOCWIN program in EPI Suite using the default molecular connectivity index method predicts a log of the organic carbon partitioning coefficient (Koc) of 10, that is seven orders of magnitude above the experimental value (AISE and CEFIC 2004). This is due to the fact that this molecule falls outside the model domain. Given that Koc has a strong influence on the prediction of partitioning to sediments, the use of the estimated Koc could lead to an overestimation of methane emissions originating in sediments. For this reason, in case of a lack of measured data for ionic substances, chemical properties can be corrected for their pH dependency with methods as those suggested by Franco et al. (2009).

3.3.2 Fate modelling

According to Webster and Mackay (2003), fate modelling outcome is uncertain due to uncertainty in chemical input data (already discussed), landscape parameters (characteristics of the evaluative environment assumed) and release rates. Concerning the release rate, it does not have any influence in our application since we are not interested in the predicted environmental concentration of the chemical, but on the fraction degraded in each compartment, which is independent of the release rate. With regard to regional variability, it certainly affects the fate model results. In our case study, we have applied USES-LCA, a model with a continental region nested in a global one. The continental scale, where chemicals are released, reflects Western Europe conditions, whereas the global one, in which the continental one is nested, reflects the Northern hemisphere. Huijbregts et al. (2003) assessed the sensitivity of the first version of USES-LCA to landscape parameters. The results are not entirely meaningful for our approach as both landscape and human exposure parameters were changed, whereas we are only interested in the sensitivity to landscape parameters. Nevertheless, the authors found that fate and exposure factors in USES-LCA are sensitive to the choice of some landscape parameters such as soil erosion rates and the dimensions of fresh water and agricultural soil compartments. In order to reduce uncertainty associated with the evaluative environment, spatially explicit fate models could be used, such as GLOBOX (Wegener Sleeswijk and Heijungs 2010), provided that the practitioner is able to identify the geographical location where the chemical is released.

3.3.3 Probabilistic analysis

Figure 4 summarizes the results of the Monte Carlo simulation, where the uncertainty associated with seven parameters is propagated. The graph shows for each chemical the probabilistic GWP_{deg} mean as well as the 2.5th and the 97.5th percentiles. It can be seen that, on the one hand, there is little uncertainty around the mean for propane released to air and

LAS released to soil. On the other hand, for melamine released to water, a wide spread of values is obtained, with 95 % of the values lying between 1.7 and 10 kg CO₂-eq per kilogram. It must be stressed that this Monte Carlo analysis has several limitations, such as the lack of sample data to correctly determine deviations around the mean for the different input parameters and the choice of probability density functions. The latter can have a remarkable influence on the obtained simulation results. Nevertheless, this exercise was useful to identify the main drivers of uncertainty in the method. We can in general conclude that uncertainty is:

- Low when modelling organic chemicals that meet these two conditions: have no nitrogen and are expected to be degraded mainly in air or soil. The reason is that the expected end product is CO₂ only.
- Medium when there is a potential for CH₄ emissions, i.e. when chemicals are expected to be degraded mainly in either the water or sediment compartments.
- High when GWP_{deg} is dominated by N₂O emissions, given the uncertainty around the IPCC emission factors for this gas.

3.4 Application in foreground and background system

The results for the nine evaluated chemicals show that emissions from degradation in the environment are relevant in the foreground system, that is, in the end-of-life stage of these particular chemicals. Nevertheless, the presented method can be used to assess the background system, for example chemical releases related to e.g. electricity consumed to produce the evaluated chemicals. The potential contribution of these emissions has not been determined in the present work, with the exception of the oxidation of methane. The latter is quite straightforward since it only

requires correcting the GWP of methane in the calculations from cradle to grave (increasing the contributions from methane by >10 %). However, extending this would require calculating GWP_{deg} for any other chemical subject to GHG formation in the environment that is recorded in the life cycle inventory. As an example, an ecoinvent dataset includes around 250 flows to air, water and soil for which GWP_{deg} factors could be calculated and incorporated in the calculations. The contribution of these background flows to the overall GWP of most datasets is a priori judged to be small when compared with those of direct emissions of CO₂, CH₄ and N₂O already included in the LCI.

4 Conclusions

A generic method to account for GHG emissions from the degradation of chemicals in the environment has been presented and tested with nine organic chemicals commonly used in agricultural and consumer products. The model has been developed for a non-site-specific situation, but it can be re-paramaterized for site-specific conditions. The method provides estimates of CH₄, CO₂ and N₂O emissions from the degradation of chemicals based on their predicted environmental fate determined using a multi-media fate model. Consistent carbon accounting rules have been provided for biogenic and fossil carbon emissions and sequestration. In addition, we have proposed to increase the GWP of methane in order to include the contribution from its oxidation to CO₂ in the atmosphere.

The application of the method with nine chemicals indicates the potential significance of GHG emissions from the degradation of chemicals in the environment, depending on the chemicals' elemental composition, initial release compartment (air, water and soil) and fate in the environment. When GHG emissions from degradation of chemicals in the environment are compared to those associated with the production of the chemicals themselves (GHG emissions from cradle to gate), they are shown to be significant, and in three of the assessed chemicals, they exceed the cradle-to-gate GHG emissions. Three aspects contributing to uncertainty were identified in the use of this method: lack of appropriate chemical-specific data, the use of a generic evaluative environment in the fate model and the uncertainty around CH₄ and N₂O emission factors. With regard to the latter, a Monte Carlo analysis showed that the highest uncertainty is expected for chemicals where GWP_{deg} is dominated by N₂O emissions.

GHG emissions from degradation of chemicals in the environment are not currently taken into account in LCA studies nor mentioned in carbon footprinting standards; omitting them can lead to a clear underestimation of the life cycle GHG emissions of chemicals, and in turn of the

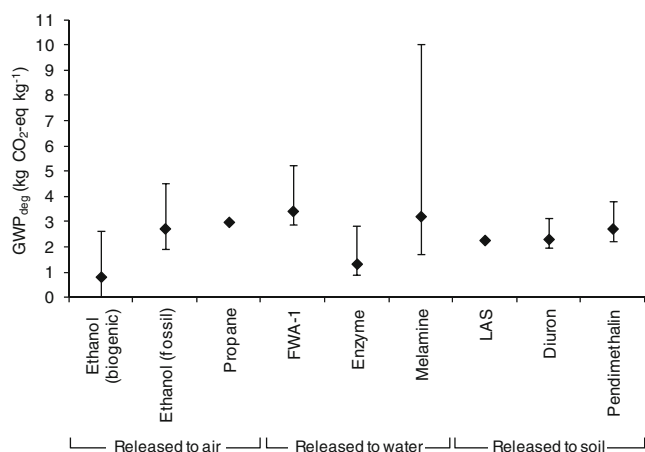


Fig. 4 Results of the Monte Carlo simulation of GWP_{deg}: probabilistic mean and 2.5th–97.5th percentiles

products using these chemicals. Such omissions can also lead to unfair comparisons of fossil-based vs. bio-based chemicals.

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